Electronic Supplementary Information for Dalton Transactions

Supporting Information

Kinetics and Mechanism of the Co(II)-assisted Oxidation of L-Ascorbic Acid by Dioxygen and Nitrite in Aqueous Solution

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Legends for Figures

Figure S1: Typical kinetic traces recorded for the reaction of complex **I** with L-ascorbic acid at 510 nm. Experimental conditions: [**I**] = 2 × 10^{-5} M, $[H_2A]_T$ = 0.28 mM, 0.1 M acetate buffer (pH 5.8, solid line) and 0.1 M TRIS buffer (pH 7.0, dashed line) at 25 ^{0}C.

Figure S2: Plots of $1/k_{obs}$ vs. $1/[H_2A]_T$ as a function of temperature. Experimental conditions: $[Co^{II}(L)(H_2O)_2]^{8-}$ = 2 x 10^{-5} M, $[H_2A]_T$ = (0.14 – 1.0) mM, 0.1 M acetate buffer (pH = 5.8).

Figure S3: Plot of k_{obs} vs. $[H_2A]_T$ for the reduction of complex **I** by L-ascorbic acid under anaerobic conditions. Experimental conditions: [**I**] = 2 x 10^{-5} M, $[H_2A]_T$ = (0.14 – 1.0) mM, 0.1 M acetate buffer (pH = 3.8) at 25 °C.

Figure S4: Plot of $\ln K_4$ versus 1/T for the reaction of complex **I** with ascorbate. Experimental conditions: [**I**] = 2 x 10^{-5} M, $[H_2A]_T$ = (0.14 – 1.0) mM, 0.1 M acetate buffer (pH = 5.8).

Figure S5: Eyring plot for reaction of complex **I** with L-ascorbic acid. Experimental conditions: [**I**] = 2 x 10^{-5} M, $[H_2A]_T$ = (0.14 – 1.0) mM, 0.1 M acetate buffer (pH = 5.8).

Figure S6: Plot of $\ln k_{obs}$ vs. pressure for the reaction between complex **I** and L-ascorbic acid. Experimental conditions: [**I**] = 2 x 10^{-5} M, $[H_2A]_T$ = 0.14 mM, 0.1 M MES buffer (pH = 5.8) at 25 °C.

Figure S7: Plot of lnK versus 1/T for the reaction of complex **I** with ascorbate. Experimental conditions: [**I**] = 2 x 10^{-5} M, $[H_2A]_T$ = (0.14 – 1.0) mM, 0.1 M TRIS buffer (pH = 7.1).

Figure S8: Eyring plot for the reaction of complex **I** with ascorbate. Experimental conditions: [**I**] = 2 x 10^{-5} M, $[H_2A]_T$ = (0.14 – 1.0) mM, 0.1 M TRIS buffer (pH = 7.1).

Figure S9: ESR spectrum of the product of the reaction between **I** and L-ascorbic acid under anaerobic conditions. Experimental conditions: [**I**] = 2.5 mM, $[H_2A]_T$ = 62.5 mM, 0.3 M TRIS buffer (pH = 7.4) at 85 K. The spectrum clearly shows the presence of Co^{II} at 2660 G (see J. Krzystek, A. Ozarowski, J. Telser, *Coord. Chem. Rev.,* 2006, **250**, 2308) and L-ascorbic acid signals between 2750 and 3000 G (see J. T. Masiakowski and A. Lund, *J. Chem. Soc., Faraday Trans.*, 1987, **83**, 1869). The spectrum was recorded using the following parameters: number of scans = 4, center of field = 3000 G, sweep width = 2500 G, resolution = 8192 points, microwave frequency = 8.9 GHz, microwave power = 1 mW, modulation frequency = 100 kHz, modulation amplitude = 2 G, time constant = 100 ms, and sweep time = 120 s.

Figure S10: Dependence of the induction period on $[H_2A]_T$. Experimental conditions: $[\mathbf{I}^{red}]$ = 2 x 10^{-5} M, $[O_2]$ = 0.2 mM, $[H_2A]_T$ = (0.035 – 0.14) mM, 0.1 M TRIS buffer (pH = 7.0) at 25 °C.

Figure S11: Eyring plot for the oxidation of reduced complex **I** by O_2. Experimental conditions: $[\mathbf{I}^{red}]$ = 2 x 10^{-5} M, $[O_2]$ = 0.6 mM, $[H_2A]_T$ = 0.035 mM, 0.1 M TRIS buffer (pH = 7.0).

Figure S12: Plot of $\ln k_{obs2}$ vs. pressure for the oxidation of the reduced form of complex **I** by O_2. Experimental conditions: $[\mathbf{I}^{red}]$ = 2 x 10^{-5} M, $[O_2]$ = 0.6 mM, $[H_2A]_T$ = 0.035 mM, 0.1 M TRIS buffer (pH = 7.0) at 35 °C.

Figure S13: Spectral changes observed during the oxidation of the reduced form of complex **I** by nitrite. Experimental conditions: $[\mathbf{I}^{red}]$ = 2 x 10^{-5} M, $[H_2A]_T$ = 0.07 mM, $[NaNO_2]$ = 100 mM, 0.1 M TRIS buffer (pH = 7.0) at 25 °C. Induction period omitted for clarity.

Figure S14: Eyring plot for the oxidation of the reduced form of complex **I** by $NaNO_2$. Experimental conditions: $[\mathbf{I}^{red}]$ = 2 x 10^{-5} M, $[H_2A]_T$ = 0.14 mM, $[NaNO_2]$ = 100 mM, 0.1 M TRIS buffer (pH = 7.0).

Figure S15: Plot of $\ln k_{obs3}$ vs. pressure for the oxidation of the reduced form of complex **I** by $NaNO_2$. Experimental conditions: $[\mathbf{I}^{red}]$ = 2 x 10^{-5} M, $[H_2A]_T$ = 0.14 mM, $[NaNO_2]$ = 80 mM, 0.1 M TRIS buffer (pH = 7.0) at 35 °C.

Figure S16: ^{15}N NMR spectrum recorded following the catalyzed oxidation of L-ascorbic acid by $Na^{15}NO_2$. Experimental conditions: $[\mathbf{I}^{red}]$ = 2 mM, $[H_2A]_T$ = 0.14 mM, $[NaNO_2]$ = 2 M, 99% D_2O at 25 °C.

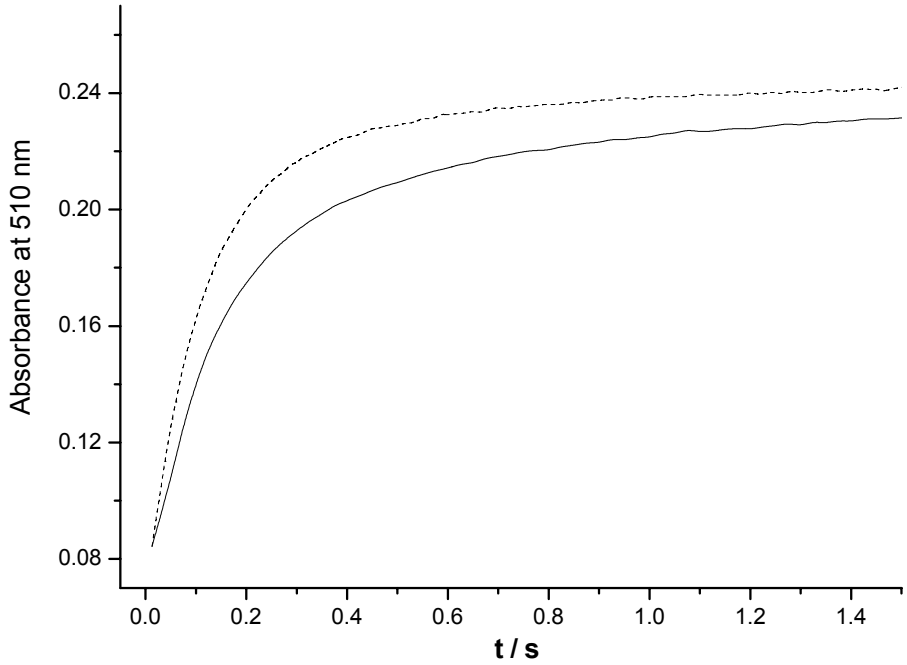
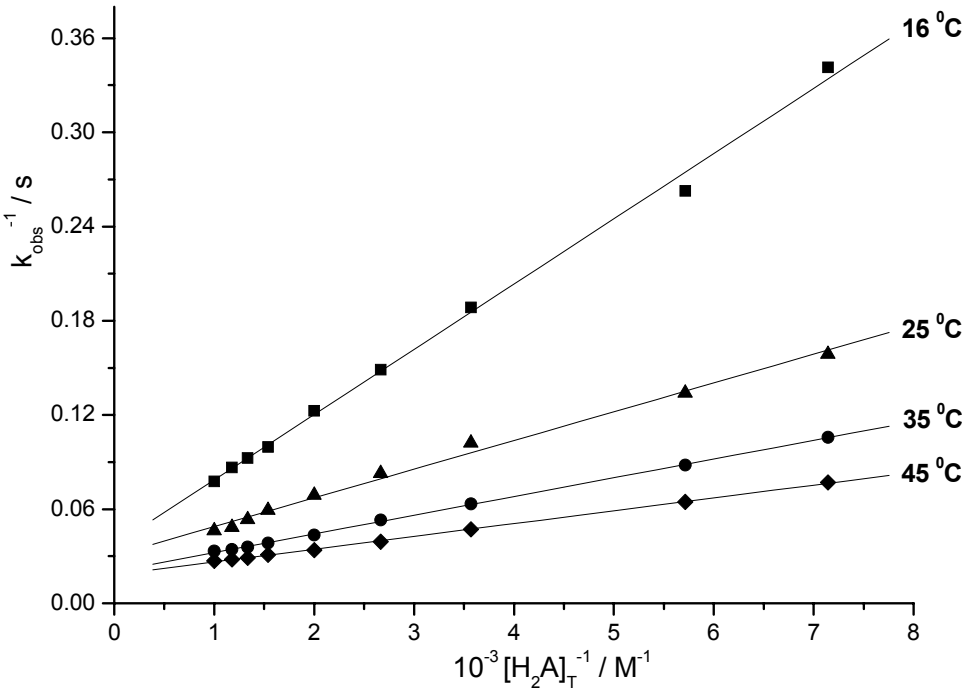


Figure S1



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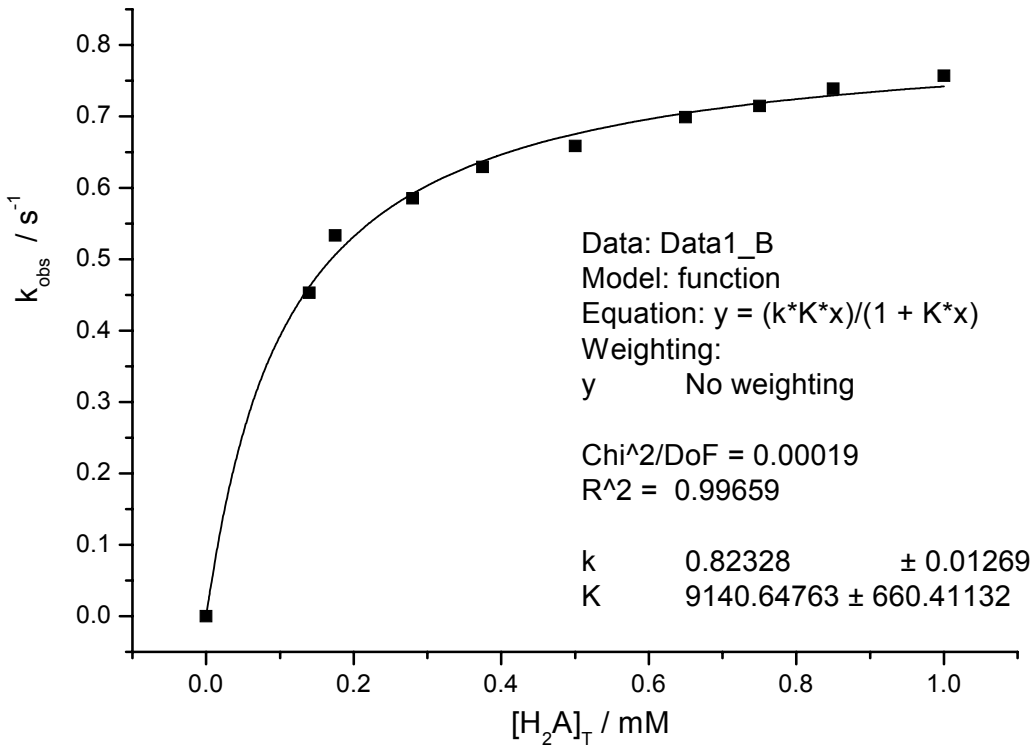

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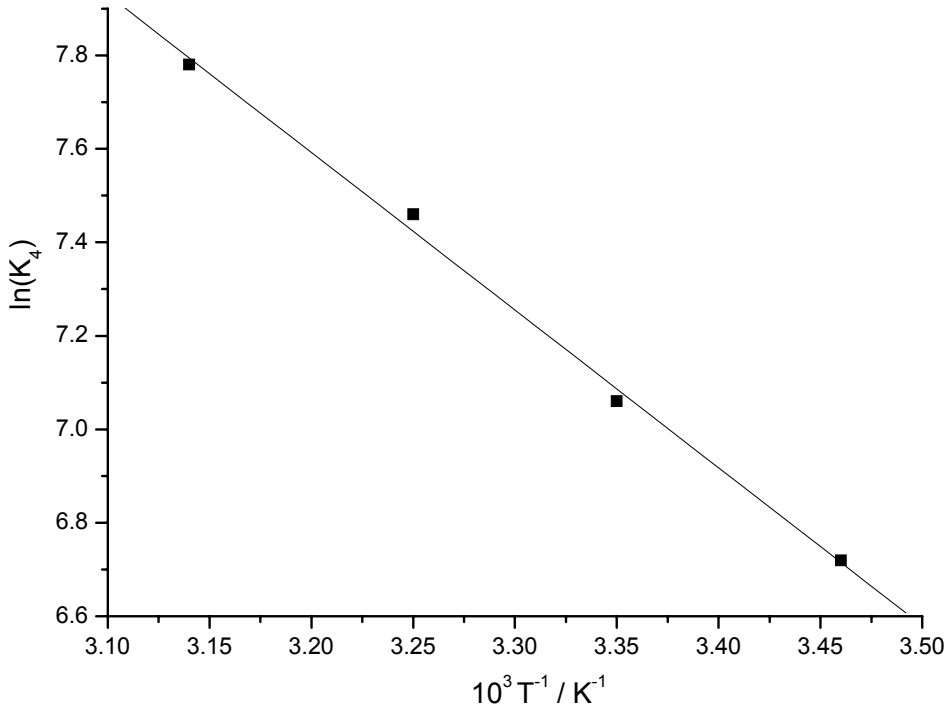

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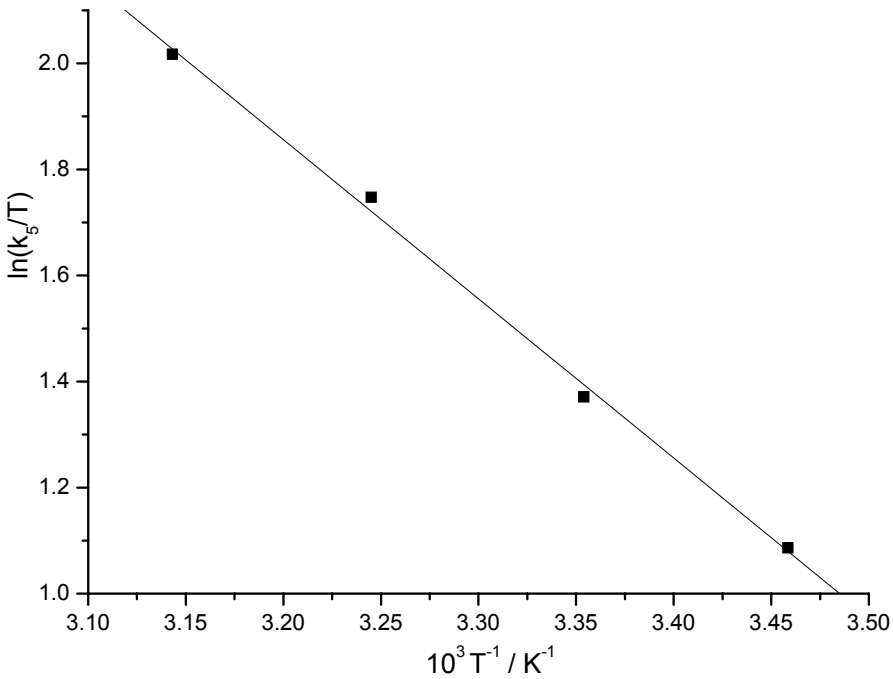

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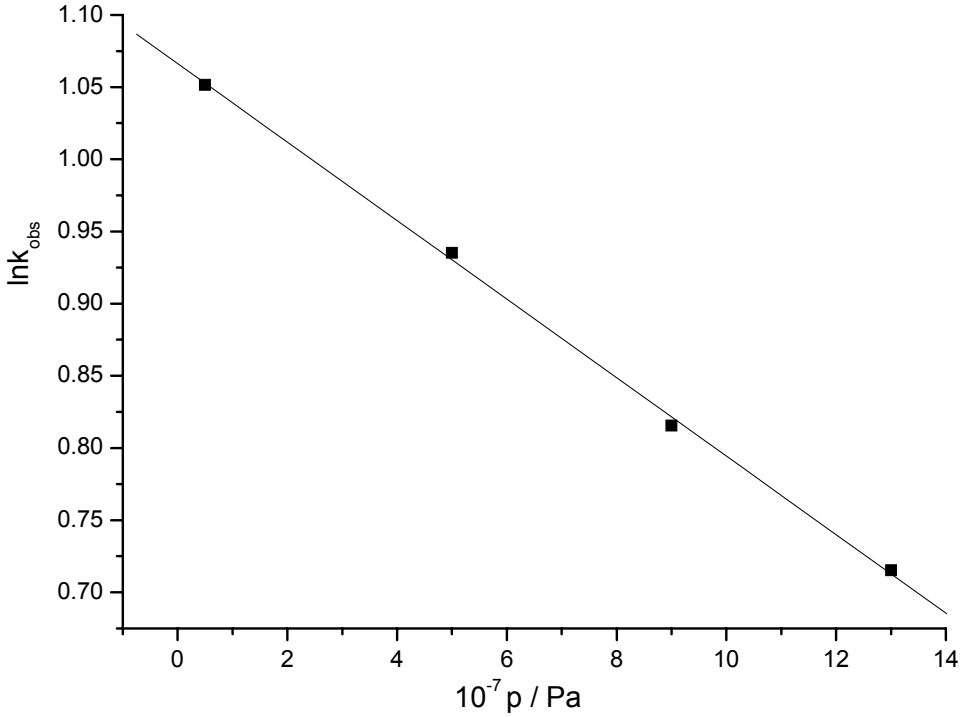

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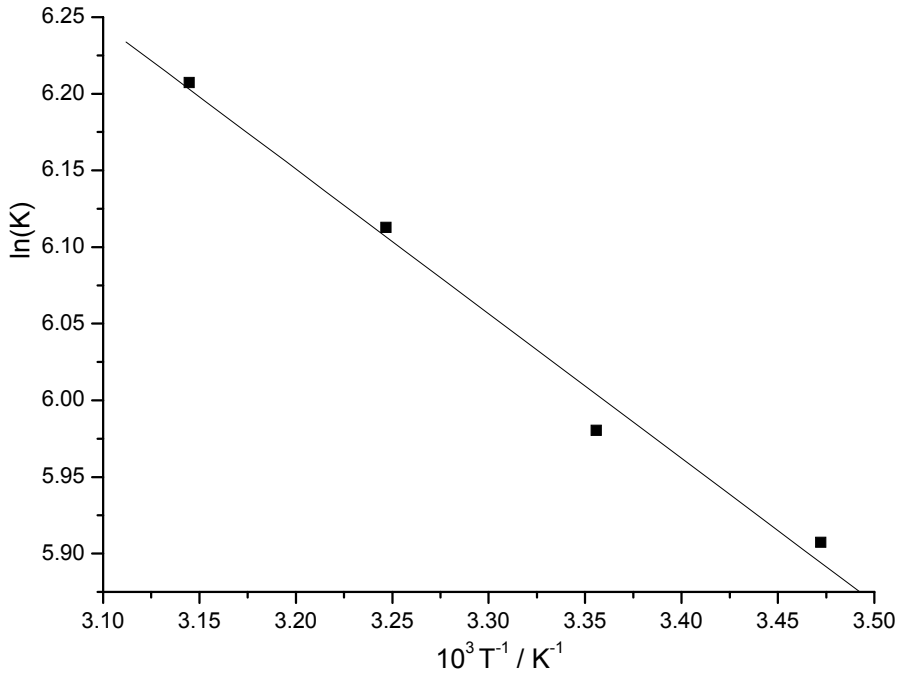

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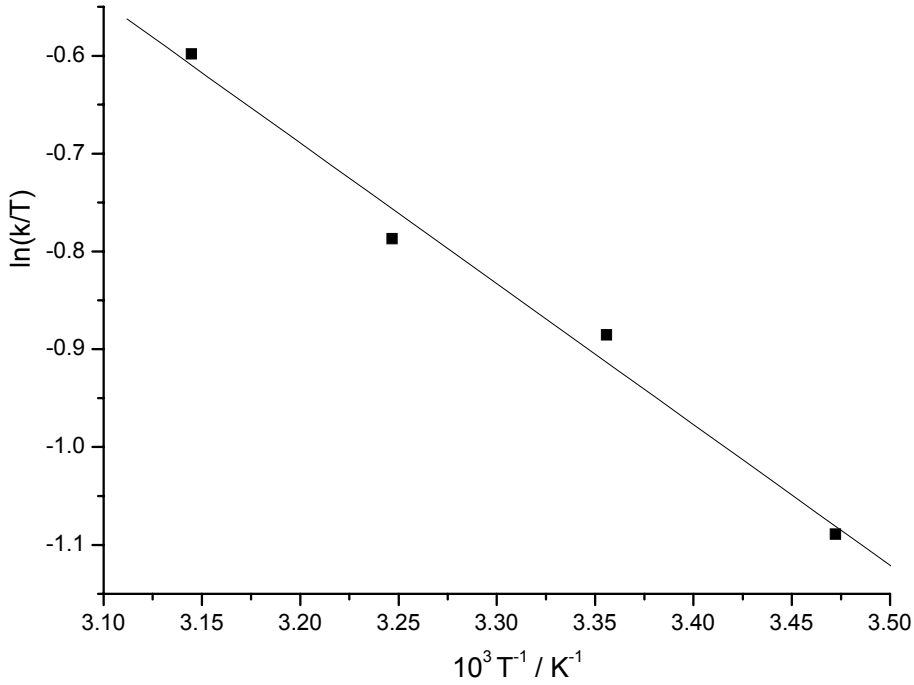

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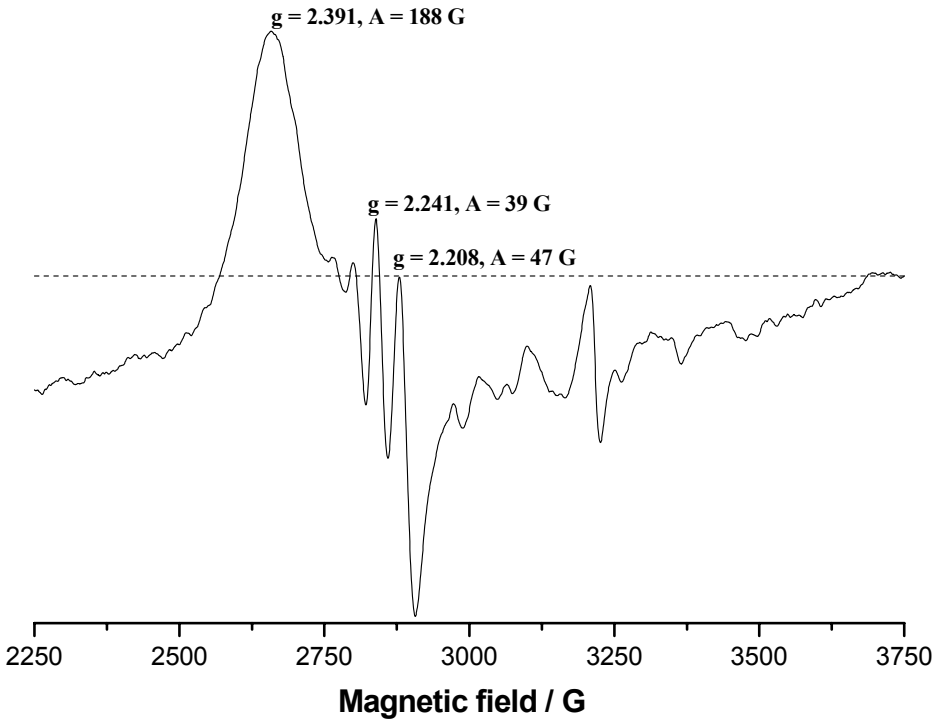

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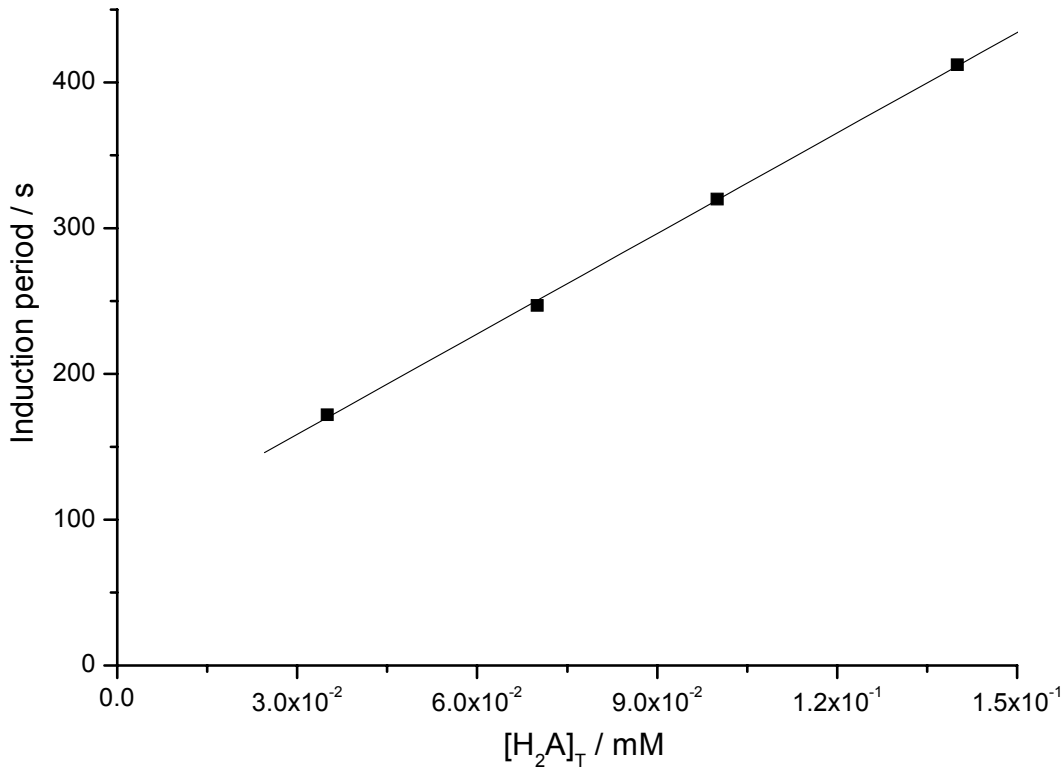

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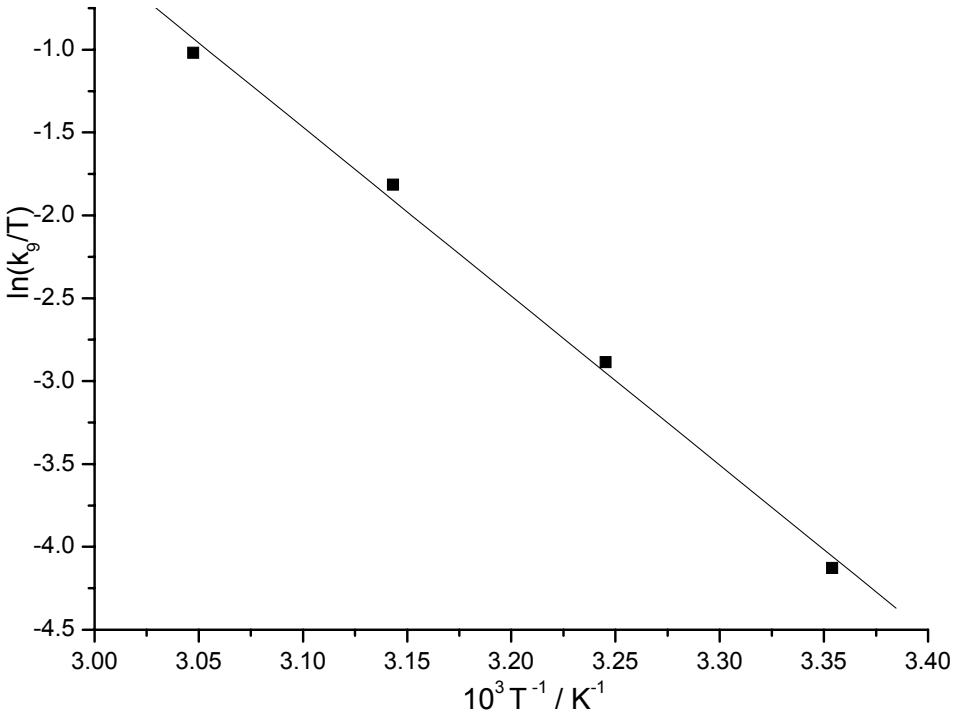

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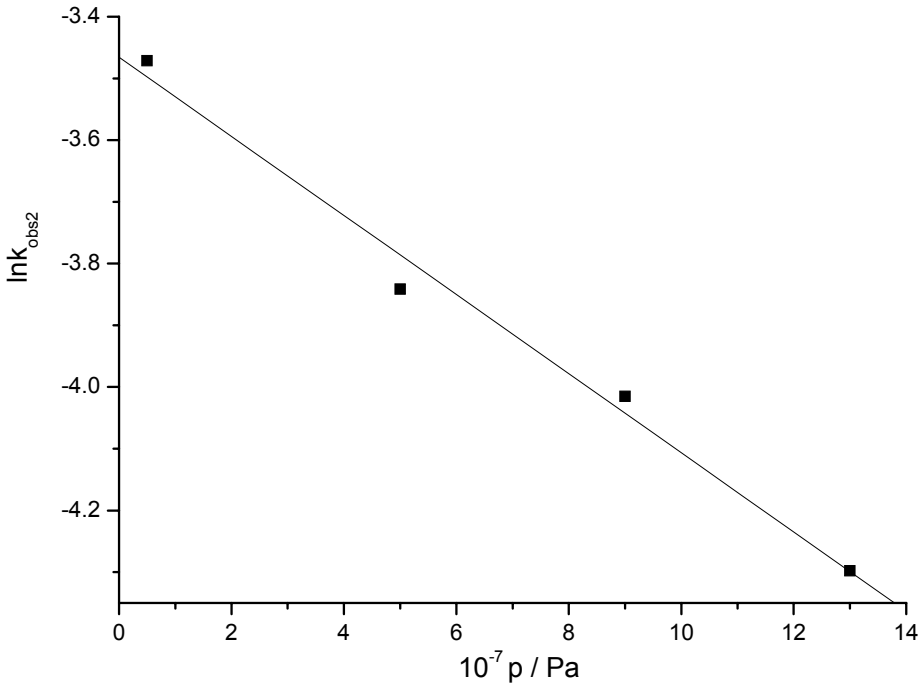

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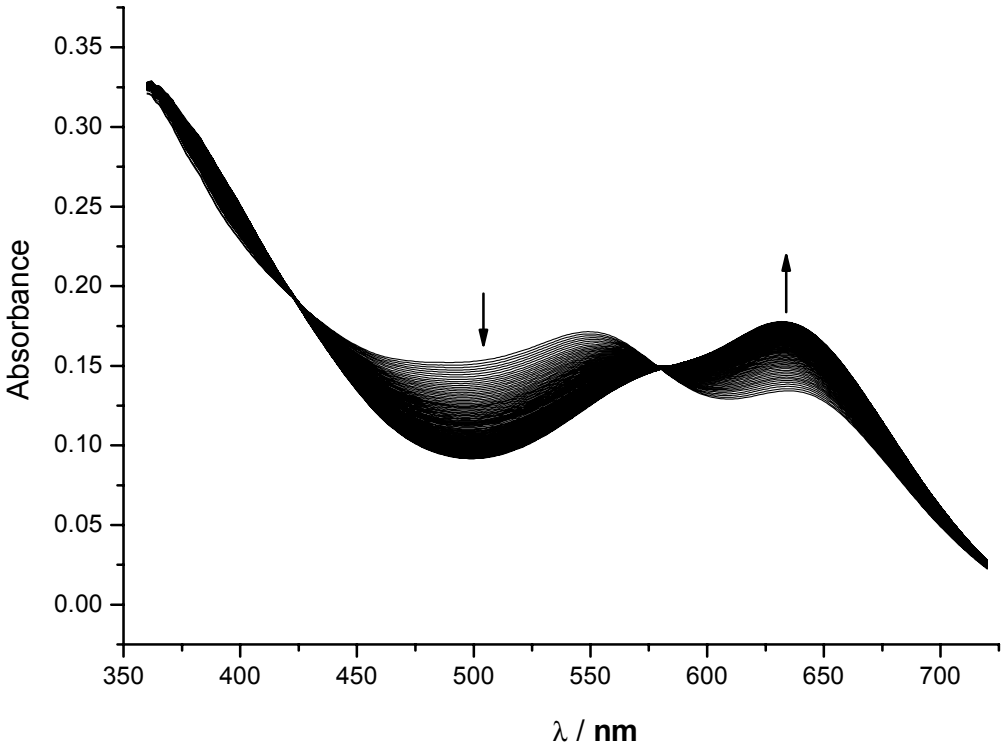

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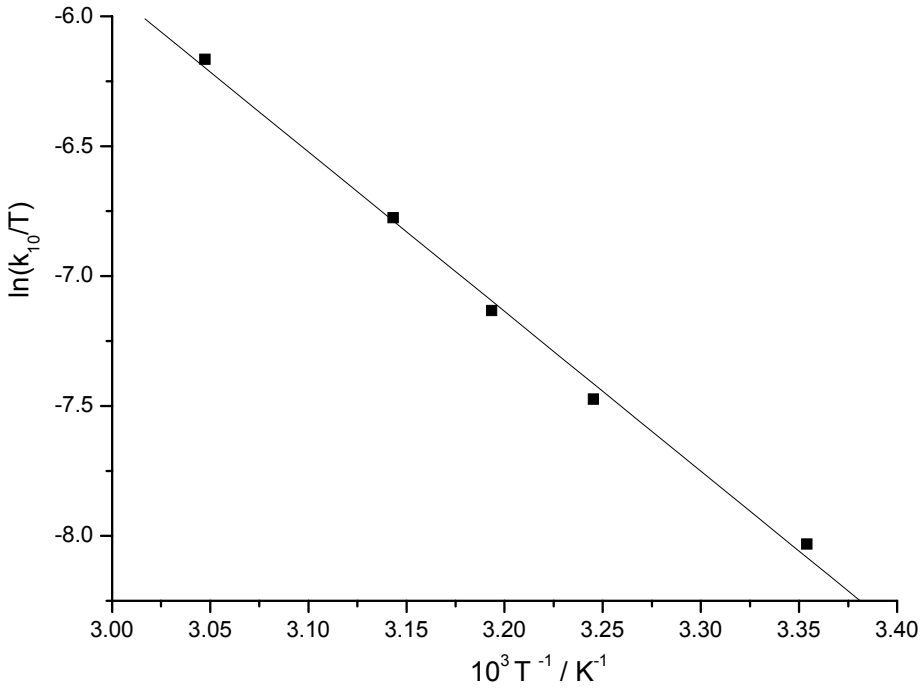

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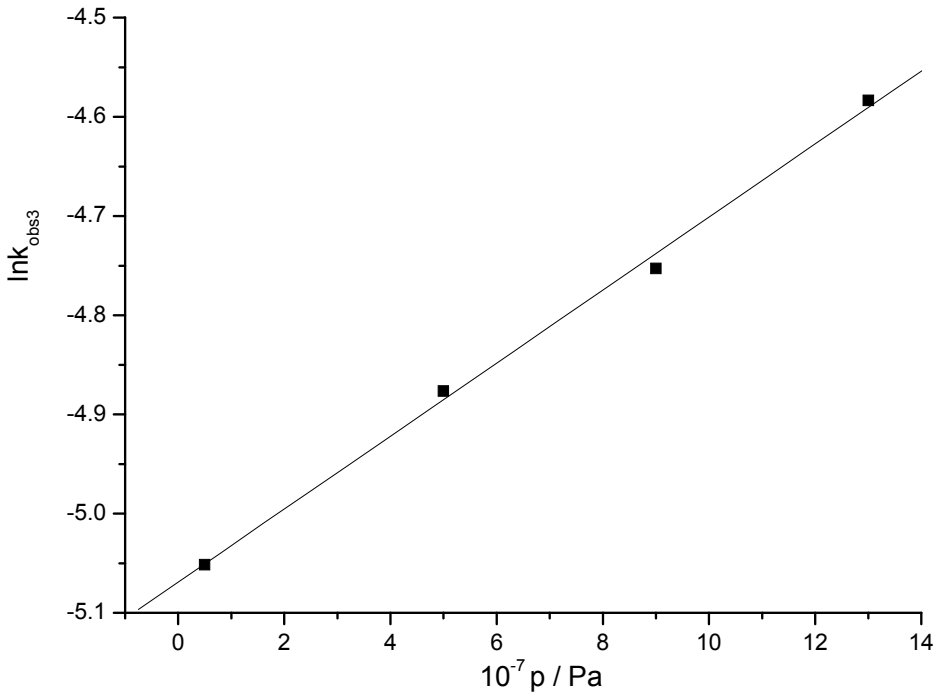

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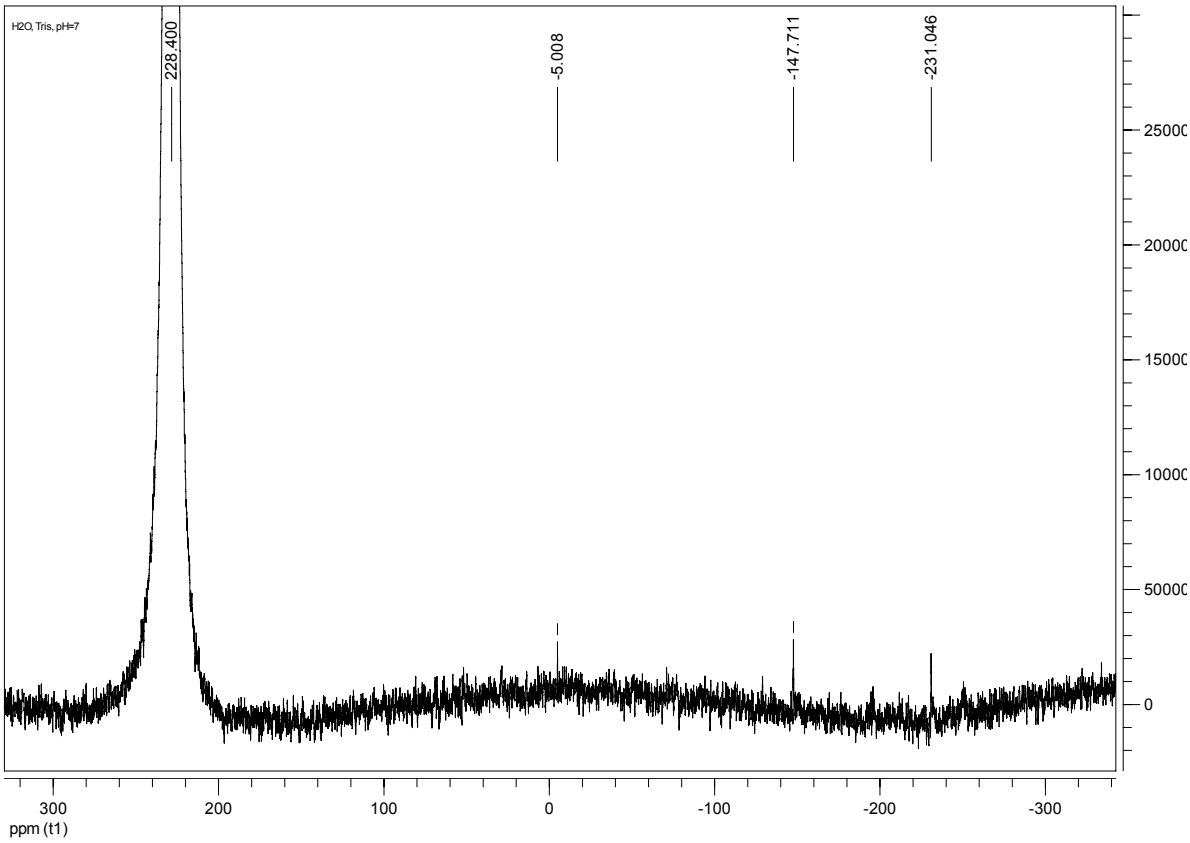

Figure S16

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